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(54) Crystalline zeolitic material, synthesis and use thereof.

(57) A new crystalline zeolitic material, designated ZSM-48, the composition of which expressed in terms of moles per 100 moles of silica, usually falls within the range:
 $(0 \text{ to } 15)RN : (0 \text{ to } 1.5)M_2/nO : (0-2)Al_2O_3 : (100)SiO_2$ wherein M is at least one cation having a valence n, RN is a C_1-C_{20} organic compound, having at least one amine functional group of $pK_a \geq 7$. ZSM-48 is characterized by the distinctive X-ray powder diffraction pattern shown in Table I, and is prepared from a reaction mixture comprising a source of silica, C_1-C_{20} organic compounds as defined above, with or without a source of alumina, and water.

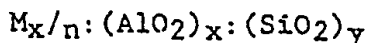
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CRYSTALLINE ZEOLITIC MATERIAL,
SYNTHESIS AND USE THEREOF

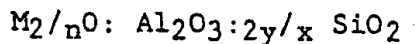
This invention relates to a new crystalline zeolitic material, to a method for synthesising it, and to its use, inter alia as organic conversion catalyst.

Many crystalline zeolites are known, in most cases as aluminosilicates. Some occur (at least so far) only in nature, for instance paulingite and merlinoite; some occur only as a result of synthesis, for instance zeolites A and ZSM-5; and some occur in both natural and synthetic forms, for instance mordenite, a synthetic counterpart of which is known as Zeolon, and faujasite, synthetic counterparts of which are known as zeolites X and Y. Counterparts are of course demonstrated as such by correspondence of their X-ray diffraction data, the indicia by means of which the individuality of a zeolite is established. Such data are a manifestation of the particular geometry of the three-dimensional lattice, formed of SiO_4 and in most cases AlO_4 tetrahedra crosslinked by the sharing of oxygen atoms and including sufficient cationic complement to balance the resulting negative charge on any AlO_4 tetrahedra, of which a zeolite may consist.

The chemical formula of an aluminosilicate zeolite is thus



where M is a cation of valence n and x and y are the number of aluminum and silicon atoms, respectively, in the unit cell (the geometric unit which repeats throughout the extent of the lattice). This expression is however frequently transmuted into the "mole ratio of oxides" form,



which is of course empirically ascertainable and thus the only formula which can be ascribed to a zeolite when

its unit cell contents are unknown. Since the only significant quantity in such a formula is the term $2y/x$, and since this term (which is almost invariably a range) can usually be satisfied by many zeolites of widely differing lattice geometry, chemical formula is not uniquely restrictive in establishing the identity of a zeolite. Furthermore, such a formula frequently expresses artefact when empirically derived, the cationic-valence/aluminum-atoms ratio deviating from unity, and it fails to provide for zeolites whose lattice structure can be brought into existence from reaction mixtures from which alumina is excluded. Moreover, both the unit cell formula and the "mole ratio of oxides" formula imply that the geometrical identity which persists between succeeding unit cells is accompanied by their compositional identity.

We have now discovered a zeolite having a lattice structure previously unknown, as evidenced by its X-ray diffraction data, which we call ZSM-48.

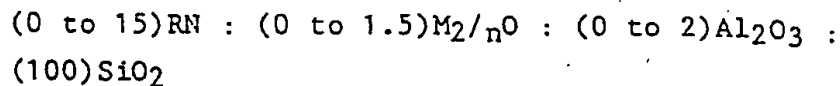
According to the present invention a crystalline zeolitic material, ZSM-48, has a lattice constituted by SiO_4 and possibly AlO_4 tetrahedra crosslinked by the sharing of oxygen atoms and characterized by the following interplanar spacings:

TABLE 1

<u>d(A°)</u>	<u>Relative Intensity</u>
11.8 \pm 0.2	W-VS
10.2 \pm 0.2	W-M
7.2 \pm 0.15	W
4.2 \pm 0.08	VS
3.9 \pm 0.08	VS
3.6 \pm 0.06	W
3.1 \pm 0.05	W
2.85 \pm 0.05	W

These values were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak heights, I , and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities, $100 I/I_0$, where I_0 is the intensity of the strongest line or peak, and d (obs.), the interplanar spacing in A, corresponding to the recorded lines, were calculated. In Table 1 the relative intensities are given in terms of the symbols W= weak, VS = very strong, W-VS and W-M = weak to very strong and weak to medium respectively. The pattern is preserved upon ion exchanges, possibly with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample and its thermal history.

In the as-synthesised form ZSM-48 usually manifests the formula in terms of mole ratios of oxides:



wherein M is at least one cation having a valence n and RN is a C₁-C₂₀ organic compound having at least one

amine functional group of $pK_a > 7$. The material of course also manifests the distinctive X-ray diffraction pattern shown in Table 1 above.

When the material contains tetrahedrally coordinated (framework) aluminum, a fraction of the amine functional groups may be protonated. The doubly protonated form, in conventional notation, would be $(RNH)_2O$ and is equivalent in stoichiometry to $2 RN + H_2O$.

Any original cations can be replaced, at least in part, by calcination and/or ion exchange. Calcination will convert as-synthesised organic cations to protons. Exchange may be performed with a metal of Groups 2 through 8 of the Periodic Table or with hydrogen ions or precursors thereof such as ammonium. Catalytically active forms of ZSM-48 can result from exchange with hydrogen, rare earth metals, aluminum, and manganese.

ZSM-48 can be prepared from a reaction mixture containing a source of silica, RN , an alkali metal oxide, e.g. sodium, water, and optionally alumina, and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

<u>REACTANTS</u>		<u>BROAD</u>	<u>PREFERRED</u>
Al_2O_3/SiO_2	=	0 to 0.02	0 to 0.01
Na/SiO_2	=	0 to 2	0.1 to 1.0
RN/SiO_2	=	0.01 to 2.0	0.05 to 1.0

OH ⁻ /SiO ₂	=	0 to 0.25	0 to 0.1
H ₂ O/SiO ₂	=	10 to 100	20 to 70
H ⁺ (added)/ SiO ₂	=	0 to 0.2	0 to 0.05

wherein RN is a C₁-C₂₀ organic compound having amine functional group of $pK_a > 7$, and maintaining the mixture at 80-250°C until crystals of the material are formed. H⁺(added) is moles acid added in excess of the moles of hydroxide added. In calculating H⁺(added) and OH values, the term acid (H⁺) includes both hydronium ion, whether free or coordinated, and aluminum. Thus aluminum sulfate, for example, would be considered a mixture of aluminum oxide, sulfuric acid, and water. An amine hydrochloride would be a mixture of amine and HCl.

ZSM-48 can be used as a catalyst in intimate combination with an additional component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such component can be introduced by exchange impregnation or physical intimate admixture, in known manner.

ZSM-48 when employed either as an adsorbent or as a catalyst should be dehydrated, at least partially, by heating to a temperature in the range of 100 to 600°C in an atmosphere, such as air, nitrogen, etc. and at atmospheric, subatmospheric or superatmospheric pressures for between 1 and 48 hours. Dehydration can also be performed at room temperature merely by placing the material in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

Preferably, crystallization is carried out under pressure in an autoclave or static bomb reactor. Thereafter, the crystals are separated from the liquid

and recovered. The reaction mixture is prepared from materials which supply the appropriate oxide. Such compositions include sodium silicate, silica hydrosol, silica gel, silicic acid, RN, sodium hydroxide, sodium chloride, aluminum sulfate, sodium aluminate, aluminum oxide, or aluminum itself. RN is a C₁-C₂₀ organic compound containing at least one amine functional group of $pK_a > 7$ and includes such compounds as C₃-C₁₈ primary, secondary, and tertiary amines, cyclic amine, such as piperidine, pyrrolidine and piperazine, and polyamines such as NH₂-C_nH_{2n}-NH₂ wherein n is 4-12.

For catalytic usage ZSM-48 may be composited with a matrix such as described in our European Specification 0,001,695. The relative proportions of ZSM-48 and matrix vary widely with the content of zeolitic material ranging from about 1 to about 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of about 2 to about 70 percent by weight of the composite.

Employing a catalytically active form of ZSM-48 containing a hydrogenation component, reforming stocks can be reformed employing a temperature between 300°C and 600°C. The pressure can be between 100 and 1000 psig but is preferably between 200 and 700 psig. The liquid hourly space velocity is generally between 0.1 and 10, preferably between 0.5 and 4 and the hydrogen to hydrocarbon mole ratio is generally between 1 and 20 preferably between 4 and 12.

ZSM-48 can also be used for hydroisomerization of normal paraffins, when provided with a hydrogenation component, e.g., platinum. Hydroisomerization is carried out at a temperature between 100° and 400°C, preferably 150° to 300°C, with a liquid hourly space velocity between 0.01 and 2, preferably between 0.25 and 0.50 employing hydrogen such that the hydrogen to

hydrocarbon mole ratio is between 1:1 and 5:1. Additionally, the catalyst can be used for olefin or aromatic isomerization employing temperatures between 50° and 400°C.

ZSM-48 can also be used as a catalyst for reducing the pourpoint of gas oils. This reduction is carried out at a liquid hourly space velocity between about 10 and about 30 and a temperature between about 400° and about 600°C. Other reactions which can be catalysed by it, with or without a metal, e.g., platinum, or palladium, include hydrogenation-dehydrogenation reactions and desulfurization reactions; olefin polymerization (oligomerization), aromatics alkylation with C₂-C₁₂ olefins or with C₁-C₁₂ alcohols, aromatics isomerization, disproportionation, and transalkylation and other organic compound conversion such as the conversion of alcohols (e.g. methanol) to hydrocarbon.

In the examples which follow ZSM-48 was prepared from reaction mixtures of the composition range:

(0.1 to 0.5)RN : (0.3 to 0.8)Na₂O : (0 to 0.02)Al₂O₃
SiO₂ : (20 to 70)H₂O

wherein RN is a C₁-C₂₀ organic compound containing at least one amine functional group of pK_a > 7.

Examples 1-17

A starting gel reaction mixture was prepared from sodium silicate (27.8% SiO₂, 8.4% Na₂O, 64% H₂O), a C₃-C₁₂ diamine compound, sodium hydroxide and water. Crystallization was carried out with stirring in a stainless steel autoclave at 160°C. After crystallization, the solids were separated by filtration and then water washed followed by drying at about 100°C. The amounts of starting material, identification of

same, product characterizations and reaction times are listed in Table 2.

The x-ray diffraction patterns of the products of Examples 5 and 7 are shown in Figures 1 and 2, respectively, and their numerical values are shown in Table 3 below. Analytical and sorption data of the products are listed in Table 4 set forth herein (Examples 18-25). Sorption was determined after dehydration at at least 200°C.

TABLE 2

Reaction Mixture Composition^a

<u>Ex.</u>	<u>Al₂O₃/</u> <u>SiO₂</u>	<u>OH/</u> <u>SiO₂</u>	<u>R</u>	<u>Days</u>	<u>Product</u>
1	0	0	None	2	Amorphous
2	0	0	C ₃ DN	3	Dense phase
3	0	0	C ₄ DN	3	ZSM-48
4	0	0	C ₅ DN	2	ZSM-48
5	0	0	C ₆ DN	2	ZSM-48
6	0	0	C ₇ DN	2	ZSM-48
7	0	0	C ₈ DN	2	ZSM-48
8	0	0	C ₉ DN	2	ZSM-48
9	0	0	C ₁₀ DN	3	ZSM-48
10	0	0	C ₁₂ DN	3	b
11	0.002	0	C ₈ DN	3	ZSM-48
12	0.005	0	C ₈ DN	2	40%, ZSM-48
					60% ZSM-11
13	0.005	0	C ₅ DN	2	10% ZSM-11
					90% ZSM-5
14	0	0.30	C ₅ DN	2	30% ZSM-5
15	0	0.15	C ₅ DN	2	15% ZSM-5
16	0	0.30	C ₈ DN	2	50% ZSM-11
17	0	0.15	C ₈ DN	2	ZSM-48
					10% ZSM-11

^a - (H₂O/SiO₂ = 40, Na/SiO₂ = 0.59, R/SiO₂ = 0.30

^b - ZSM-48 and second unidentified component

TABLE 3
X-RAY DIFFRACTION DATA OF ZSM-48.

<u>Product of Example 5</u>			<u>Product of Example 7</u>		
2 θ	D	INT	2 θ	D	INT
7.45	11.87	14	7.42	11.91	15
8.65	10.22	6	8.60	10.28	7
12.26	7.22	2	12.26	7.22	3
14.46	6.13	1	14.42	6.14	2
15.06	5.88	6	15.06	5.88	6
17.45	5.08	1	17.47	5.08	1
19.05	4.66	4	19.01	4.67	4
21.13	4.20	76	21.18	4.19	84
22.74	3.91	100	22.77	3.91	100
24.74	3.60	12	24.73	3.60	13
25.70	3.47	2	25.75	3.46	2
26.10	3.41	3	26.15	3.41	3
26.36	3.38	3	26.38	3.38	4
27.60	3.23	1	27.65	3.23	1
28.83	3.10	2	28.84	3.10	3
31.32	2.86	11	31.33	2.86	13
32.83	2.73	2	32.88	2.72	2
34.05	2.63	2	34.05	2.63	2
35.44	2.53	1	35.48	2.53	1
36.30	2.47	2	36.30	2.47	3
37.66	2.39	3	37.70	2.39	3
38.40	2.34	2	38.40	2.34	2
43.18	2.10	2	43.25	2.09	3
43.77	2.07	3	43.83	2.07	4
44.58	2.03	1	44.82	2.02	1
45.12	2.01	1			
46.30	1.96	2	46.37	1.96	2
49.22	1.85	2	49.22	1.85	2
50.07	1.82	1	50.12	1.82	1
51.56	1.77	1	51.57	1.77	1

Review of the data in Table 2 shows that (1) no ZSM-48 crystallized in the absence of the diamine. (Ex. 1) (2) C₄-C₁₀ diamines yielded ZSM-48 in good crystallinity (Ex. 3-9) (3) ZSM-48 can be prepared with added aluminum although with these diamines, ZSM-5 (Ex. 13) or ZSM-11 (Ex. 12) may be preferred, depending on reaction mixture composition, and (4) that an optimum OH/SiO₂ ratio exists near zero.

Example 26

This example shows that very different types of amines are effective in ZSM-48 synthesis. A reaction mixture was prepared as in Examples 1-17 except that the amine was N,N'-bis(3-aminopropyl) piperazine. Mole ratios of reactants were as follows:

Al ₂ O ₃ /SiO ₂	=	0
H ₂ O/SiO ₂	=	40
OH/SiO ₂	=	0
Na/SiO ₂	=	0.6
R/SiO ₂	=	0.3

after 2 days at 160°C in a stirred autoclave, ZSM-48 was obtained in good crystallinity.

Example 27

This example shows that simple amines are effective in ZSM-48 synthesis. A reaction mixture was prepared according to the procedures of Examples 1-17 except that the organic was n-hexylamine. The reaction mixture composition had the following mole ratios:

$\text{Al}_2\text{O}_3/\text{SiO}_2$	=	<0.01
$\text{H}_2\text{O}/\text{SiO}_2$	=	40
OH/SiO_2	=	0
Na/SiO_2	=	0.6
R/SiO_2	=	0.3

Crystallization was conducted in a stirred autoclave at 160°C for 2 days. The crystalline product was ZSM-48, contaminated with a minor portion of β -cristobalite.

Example 28

The product of Example 7 was tested for relative hexane cracking activity (\mathcal{J} -value), and for constraint index (the ratio of the rate constant for cracking of n-hexane to that of 3-methylpentane) at 510 and at 538°C*. At 510°C, the ZSM-48 product exhibited a constraint index of 5.3 and an \mathcal{J} of 5.0. At 538°C, the C.I. was 3.4.

* The \mathcal{J} -test is described in a letter to the editor entitled 'Superactive Crystalline Aluminosilicate Hydrocarbon Cracking Catalysts' by P.B. Weisz and J. N. Miale, Journal of Catalysis, Vol. 4, pp. 527-529 (August 1965). The constraint index test is described in U.S. Patent 4,107,224.

TABLE 4
Characterization Data

Example	H ₂ O x*	SiO ₂ /Al ₂ O ₃	Composition ^a			Sorption, % (25°C) ^b	
			Al	Na	N	NC6	CyC6
18	(Product of Example 4)	870	0.23	0.8	6.9	3.6	3.7
19	(Product of Example 5)	1320	0.15	0.7	6.2	3.3	2.5
20	(Product of Example 6)	1340	0.15	0.5	5.6	3.0	3.0
21	(Product of Example 2)	400	0.51	0.4	6.2	3.4	-
22	(Product of Example 7)	1170	0.17	0.7	5.9	3.0	3.6
23	(Product of Example 8)	1190	0.17	0.5	5.0	2.7	-
24	(Product of Example 9)	1290	0.17	0.5	5.2	2.7	-
25	(Product of Example 3)	910	0.17	0.3	1.4	2.6	3.3
Average							3.1

a - Per 100 SiO₂

b - Ilydrocarbons, 20mm; water, 12mm

c - Diamine (per 100 SiO₂)

As previously mentioned, the X-ray diffraction pattern is preserved upon ion exchanges, possibly with minor shifts in spacing and variation in relative intensity. We have found that the calcined, sodium-exchanged form of ZSM-48 exhibits the following interplanar spacings:

TABLE 5

<u>D(A°)</u>		<u>Relative Intensity</u>
11.8 \pm	0.2	W - VS
10.2 \pm	0.2	W - M
7.2 \pm	0.15	W - VS
4.2 \pm	0.08	VS
3.9 \pm	0.08	VS
3.6 \pm	0.06	W
3.1 \pm	0.05	W
2.85 \pm	0.05	W

The relative intensities are given by the same symbols as used in Table 1 above.

The effect of calcination and sodium exchange is illustrated by Examples 29 and 30 below.

Example 29

The dried product of Example 5 (two grams) was calcined in nitrogen for 2.5 hours at 550°C followed by cooling in nitrogen for about 30 minutes. The calcined sample was ion exchanged three times with stirring at 80°C with 100 ml 2N sodium nitrate, for 2 hours each time. The sodium form sample was filtered, washed with water and dried under a heat lamp for about 30 minutes.

The X-ray diffraction data of the calcined sodium-exchange form is given below in Table 6, and the X-ray scan is shown in Figure 3 of the accompanying drawings.

TABLE 5X-Ray Diffraction Data of ZSM-48Product of Example 29

(Na-Exchanged)

2 θ	D	INT
7.56	11.69	43
8.74	10.12	18
10.66	8.30	1
12.33	7.18	7
13.09	6.76	1
13.58	6.52	1
14.51	6.10	6
15.15	5.85	12
16.92	5.24	1
17.52	5.06	2
18.12	4.90	3
18.65	4.76	2
19.02	4.67	3
19.36	4.58	1
19.82	4.48	1
20.54	4.32	5
21.13	4.20	100
21.82	4.07	4
22.47	8.96	12
22.93	3.88	72
23.82	3.74	3
24.18	3.68	3
24.56	3.62	5
24.96	3.57	8
25.34	3.51	6
25.74	3.46	8
26.11	3.41	3
26.51	3.36	5
27.96	3.19	1
29.01	3.08	2
30.66	2.92	1
31.35	2.85	12
31.64	2.83	1

TABLE 6 (cont'd)

32.61	2.76	2
32.89	2.72	2
33.56	2.67	1
34.11	2.63	2
35.66	2.52	1
36.20	2.48	3
36.57	2.46	2
37.05	2.43	2
37.48	2.40	2
37.89	2.37	3
38.38	2.35	2
38.92	2.31	1
40.31	2.24	1
43.02	2.10	4
44.03	2.06	2
45.05	2.01	1
45.96	1.97	1
46.48	1.95	1
48.11	1.89	1
49.28	1.85	1
51.69	1.77	1

Example 30

The dried product of Example 7 (2 grams) was calcined for 4 hours in nitrogen at 550°C followed by cooling in ammonium gas for about 30 minutes. The calcined sample was exchanged twice with 100 ml 1N ammonium nitrate solution, at 60°C with stirring for about 2 hours for each exchange. The ammonium form sample was then washed, dried and again calcined for 2 hours at 550°C in nitrogen and cooled in nitrogen. This calcined sample was ion-exchanged 3 times with stirring at 60°C in 2N sodium nitrate solution. The sodium form sample was filtered, washed with water and dried under a heat lamp for about 30 minutes.

The X-ray diffraction data of the calcined sodium ion-exchanged form is given below in Table 7, and the X-ray scan is shown in Figure 4 of the accompanying drawings.

TABLE 7X-Ray Diffraction Data of ZSM-48Product of Example 30
(Na-Exchanged)

2 θ	D	INT
7.53	11.74	48
8.71	10.15	18
10.70	8.27	1
12.30	7.20	7
13.04	6.79	1
13.62	6.50	1
14.52	6.10	8
15.10	5.87	14
16.90	5.25	1
17.53	5.06	3
18.10	4.90	3
18.64	4.76	2
19.06	4.66	2
19.62	4.52	2
20.07	4.42	2
20.47	4.34	5
21.10	4.21	100
21.93	4.05	7
22.41	3.97	12
22.91	3.88	77
23.82	3.74	4
24.16	3.68	4
24.52	3.68	6
24.90	3.58	10
25.32	3.52	7
25.72	3.46	8
26.10	3.41	4
26.50	3.36	6
29.04	3.07	2
30.71	2.91	1
31.35	2.85	12
32.55	2.75	1
32.84	2.73	2
33.56	2.67	1
34.14	2.63	2
35.64	2.52	2
36.20	2.48	3
36.59	2.46	2
37.00	2.48	2
37.40	2.40	2
37.85	2.38	4
38.34	2.35	3
38.86	2.32	1
40.33	2.24	1
43.04	2.10	4
44.06	2.06	2

CLAIMS:

1. A crystalline zeolitic material having a lattice comprising SiO_4 tetrahedra crosslinked by the sharing of oxygen atoms and characterized by the following interplanar spacings:

<u>d(A°)</u>	<u>Relative Intensity</u>
11.8 ± 0.2	W-VS
10.2 ± 0.2	W-V
7.2 ± 0.15	W
4.2 ± 0.08	VS
3.9 ± 0.08	VS
3.6 ± 0.06	W
3.1 ± 0.05	W
2.85 ± 0.05	W

2. A crystalline zeolitic material according to claim 1 the lattice of which also comprises AlO_4 tetrahedra.

3. A crystalline zeolitic material according to claim 1 or claim 2 which has the formula, in terms of mole ratios:

$0-15 \text{ RN} : 0-1.5 \text{ M}_2/\text{RO} : 0-2 \text{ Al}_2\text{O}_3 : 100 \text{ SiO}_2$
in which M is at least one cation of valance n and RN is an organic compound having at least one amine functional group of $\text{pK}_a \geq 7$.

4. A crystalline zeolitic material according to claim 3 wherein RN is of the formula $\text{H}_2\text{N} - \text{C}_x\text{H}_{2x} - \text{NH}_2$ in which x is from 4 to 12.

5. A crystalline zeolitic material according to claim 3 wherein RN is of the formula $\text{C}_x\text{H}_{2x+1} - \text{NH}_2$ in which x is from 1 to 20.

6. A crystalline zeolitic material according to any of claims 2 to 5 which contains hydrogen, ammonium or rare earth cations.

7. A crystalline zeolitic material according to any of claims 2 to 6 in which the molar ratio of silica to alumina is from 800 to 15000.

8. A method for preparing the crystalline zeolitic material claimed in claim 1 which comprises preparing a reaction mixture containing a source of a silica, an alkali metal oxide, RN, water and alumina, and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

$\text{Al}_2\text{O}_3/\text{SiO}_2$	= 0 to 0.02
Na/SiO_2	= 0 to 2.0
OH^-/SiO_2	= 0 to 0.25
$\text{H}^+(\text{added})/\text{SiO}_2$	= 0 to 0.2
$\text{H}_2\text{O}/\text{SiO}_2$	= 10 to 100
RN/SiO_2	= 0.01 to 2.0

wherein RN is a C₁-C₂₀ organic compound containing amine functional groups of $\text{pK}_a \leq 7$ and maintaining said mixture at crystallization temperature until crystals are formed.

9. A method according to claim 8 wherein said reaction mixture has the composition:

$\text{Al}_2\text{O}_3/\text{SiO}_2$	0 to 0.01
Na/SiO_2	0.1 to 1.0
OH^-/SiO_2	0 to 0.1
$\text{H}^+(\text{added})/\text{SiO}_2$	0 to 0.05
$\text{H}_2\text{O}/\text{SiO}_2$	20 to 70
RN/SiO_2	0.05 to 1.0

10. A method according to claim 8 or claim 9 in which RN is of the formula $\text{H}_2\text{N} - \text{C}_x\text{H}_{2x} - \text{NH}_2$ in which x is from 4 to 12.

11. A method according to claim 8 or claim 9 in which RN is of the formula $\text{C}_x\text{H}_{2x+1} - \text{NH}_2$ in which x is from 1 to 20.

12. A method according to any of claims 8 to 11 in which said temperature is in the range 80 to 250°C.

13. A process of converting an organic charge which comprises contacting the charge under conversion conditions with a catalyst comprising the material claimed in any of claims 1 to 7.

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FIGURE 1

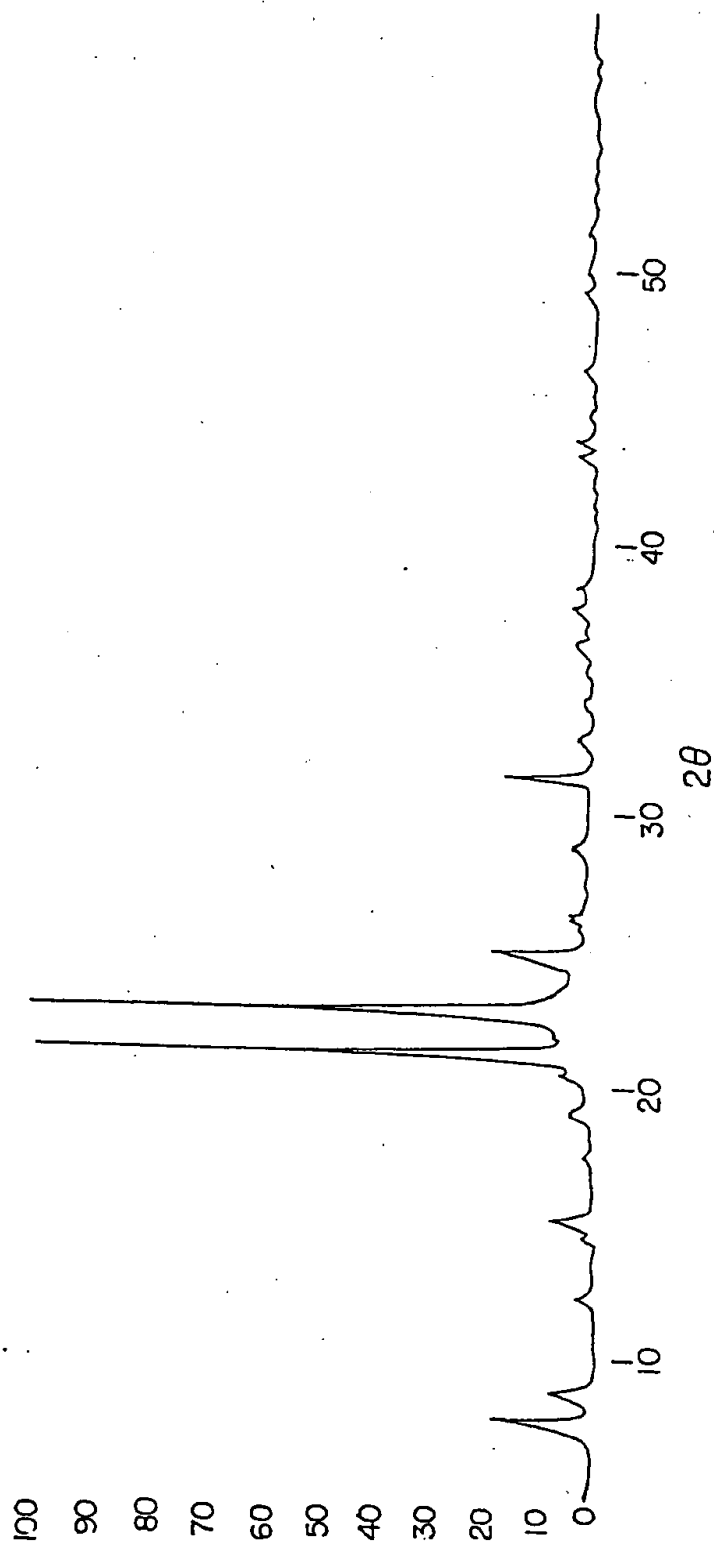


FIGURE 2

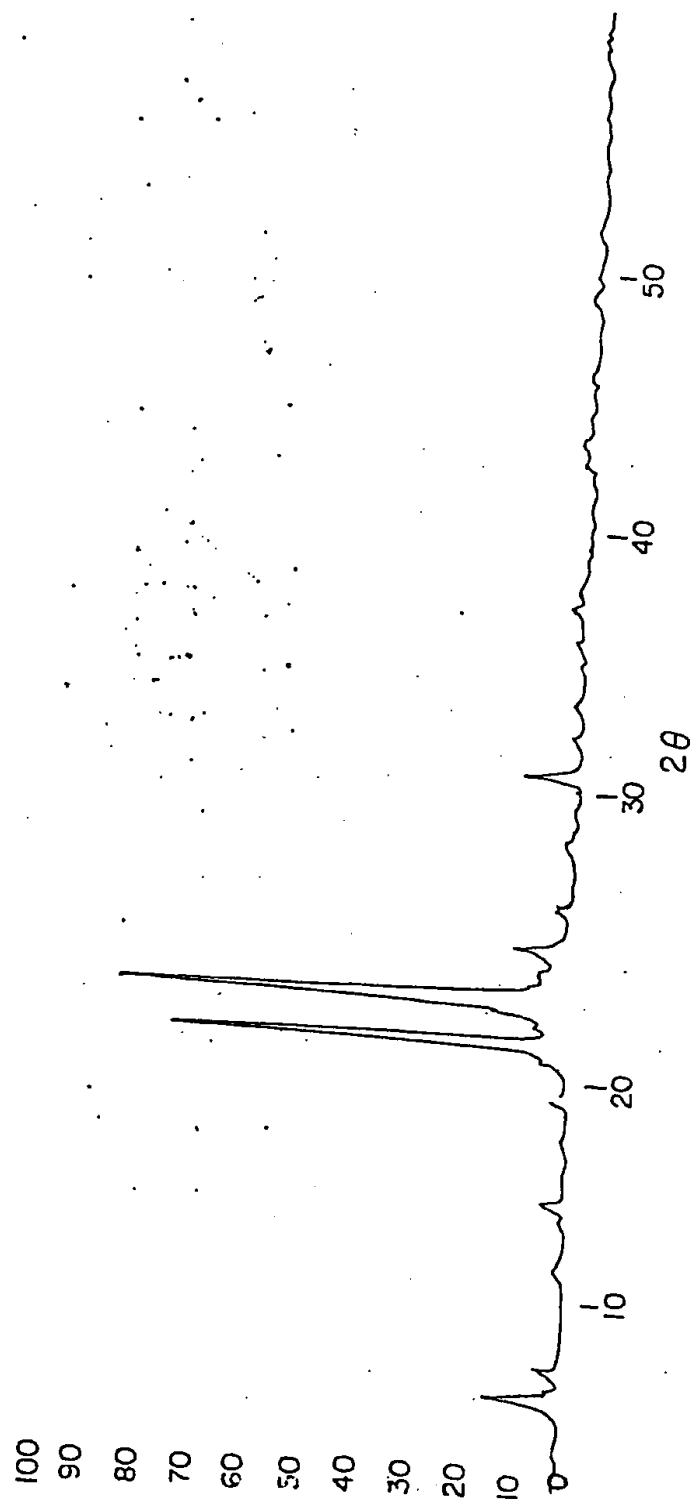


FIGURE 3

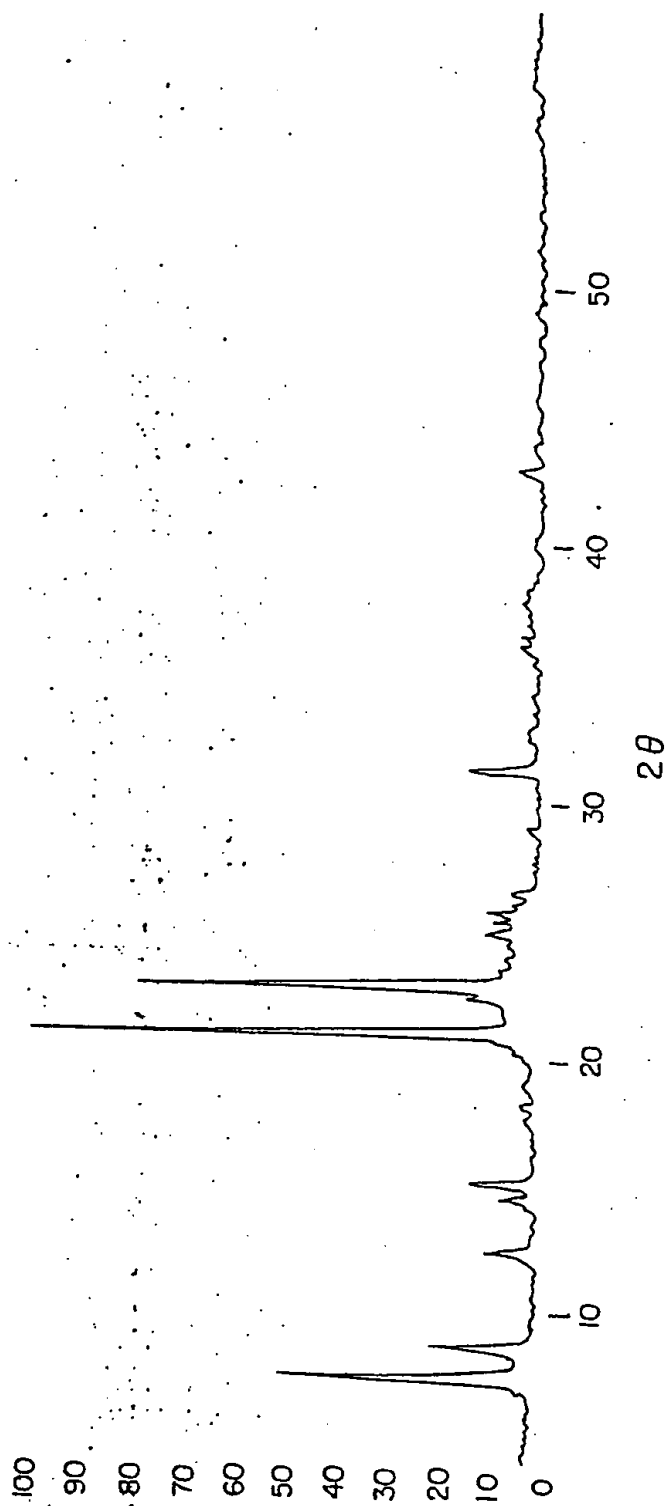
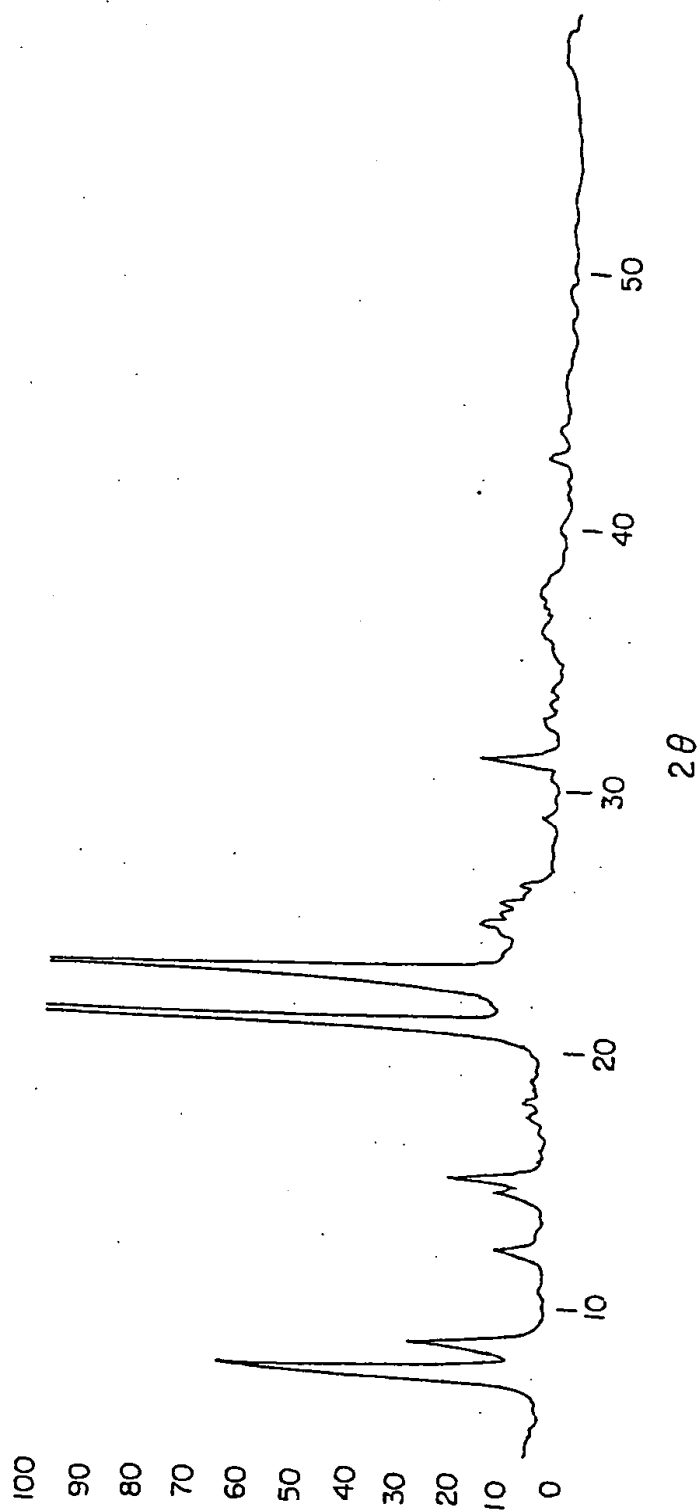


FIGURE 4





European Patent
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EUROPEAN SEARCH REPORT

0015132

Application number

EP 80 30 0463

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D, P	<u>EP - A1 - 0 001 695</u> (MOBIL OIL) ---		C 01 B 33/28 B 01 J 29/28
D	<u>US - A - 4 107 224</u> (MOBIL OIL) ---		
A	<u>US - A - 4 108 881</u> (MOBIL OIL) ---		
A	<u>US - A - 4 046 859</u> (MOBIL OIL) ---		
A	<u>US - A - 4 016 245</u> (MOBIL OIL) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			B 01 J 29/00 C 01 B 33/28 C 07 C 2/00 C 07 C 4/00 C 07 C 5/00 C 10 G 11/05 C 10 G 35/095
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search Berlin		Date of completion of the search 06-05-1980	Examiner KESTEN